

Vibrational Projection Analysis: New Tool for Quantitatively Comparing Vibrational Normal Modes of Similar Molecules

ANTHONY K. GRAFTON,* RALPH A. WHEELER

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019

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ABSTRACT: A new method for quantitatively comparing calculated vibrational modes is described that relies on projecting the vectors describing the normal modes of one molecule onto those of a basis molecule. The procedure virtually automates the assignment of vibrational modes from one molecule to a second, structurally similar one. We illustrate the concept by using the classical Wilson modes of benzene as a basis for describing normal modes of the monosubstituted benzene derivatives phenol, phenol-*d*5, and phenol radical cation. These examples demonstrate the method's power for accurately assigning and comparing the normal modes of molecules perturbed by chemical substitution, isotopic substitution, or oxidation state. The vibrational projection analysis method—a special case of vector projection analysis—is compared and contrasted with total energy distribution analysis, perhaps the most commonly used technique for quantitatively comparing vibrational modes, and is found superior in each case when comparing normal modes. Vibrational projection analysis need not be limited to single molecules and quantum calculations, because normal modes may be obtained for much larger systems using molecular mechanics or molecular dynamics techniques. The method should therefore

* *Permanent address:* Department of Science, Campbellsville University, 1 University Drive, Campbellsville, KY 42718

Correspondence to: R. A. Wheeler

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prove useful for interpreting the normal modes of ordered periodic solids and structures perturbed by noncovalent contacts, including proteins and polymers. The method may also prove useful in evaluating new computational methods by allowing direct, quantitative comparison of the vibrational modes obtained from different techniques. The power of this technique will make vibrational projection analysis a valuable tool for computational chemists as well as those using calculations to complement vibrational spectroscopic measurements.
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Introduction

Advances in computational chemistry over the past 20 years have made the calculation of vibrational frequencies and vibrational modes of small molecules routine and promise access to the same data for increasingly large and complicated structures. Analytical gradient methods¹ are now incorporated in most quantum chemistry programs and allow the accurate determination of minimum energy geometries as well as vibrational frequencies and modes for many molecules. Computer programs are also becoming available to calculate normal vibrational modes of proteins based on molecular mechanics calculations.^{2,3} These stunning advances in computational technology have been accompanied by equally remarkable progress in spectroscopic methods. Collecting vibrational spectra for small molecules is now routine and advances at the forefront of vibrational spectroscopy make it possible to measure vibrational frequencies for large, complex structures such as proteins^{4,5} and polymers.^{6,7} Vibrational difference spectroscopy, for example, now provides the means to compare experimental spectra for oxidized and reduced protein side-chains directly.⁸ The easy access to and convenience of quantum chemical, molecular mechanics, and molecular dynamics computer programs, coupled with the amazing progress in computational and experimental methods, means that calculated vibrational frequencies and modes are now an important complement to experimental spectral measurements. It also means data can be computed rapidly and in great quantities, even for very large systems. For example, even a relatively small calculation for the simple, highly symmetrical benzene molecule can produce nearly two million bytes of data. The proper analysis of and conve-

nient comparisons among such copious data can be both difficult and time consuming. In this contribution, we show that computed vibrational modes can be quickly and quantitatively assigned and compared using a simple but powerful new technique that relies on vector projection. The vibrational projection analysis method described here is also compared with complementary methods for comparing vibrational modes, such as total energy decompositions (TED)⁹ and graphical visualization.

Vibrational spectra can be used to infer such things as changes in bonding, electronic state, or local environment, but drawing these inferences from experimental or theoretical data is often a complicated matter. Frequently, it is necessary to compare the spectra of two systems and note changes in the vibrational frequencies. However, mode mixing and related phenomena induced by a perturbation can make this process difficult, especially if the initial mode assignments are uncertain. Even the computational chemist, with pictorial and animated normal modes of vibration available, can find that confidently matching the modes of similar systems is tedious at best, and can become quite difficult if the two systems differ in such things as chemical substituents or oxidation states, which can dramatically affect the descriptions of vibrational modes. The importance of comparing and assigning vibrational modes has been noted recently by others, who have automated the process using energy distributions.¹⁰ We present here an alternate method, which is both simpler and more powerful, and we demonstrate its utility with several examples.

The TED is the numerical method currently used most often by computational chemists to help match vibrational modes between different molecules.¹⁰ The TED was originally developed to provide a quantitative breakdown of the energetic contributions of a molecule's internal coordinates

to each of the vibrational modes. Using this method, one could describe a vibration of a molecule such as benzene as 95% C—H stretch and 5% C—C stretch. TED calculation has been incorporated in commonly used programs such as GAMESS,¹¹ and is essentially the only quantitative tool available to describe normal modes.

If used for its intended purpose—describing individual normal modes of a single system—then TED analysis can be quite useful. Although TED analysis was never claimed as a replacement for applications in which the eigenvectors are required, computational chemists have nevertheless come to rely on TEDs to assist in the comparison of vibrational modes from different systems and, in this regard, TED analysis has some important shortcomings. First, and least seriously, the results of the analysis can depend on the user's choice of internal coordinates. Methods have been proposed for selecting internal coordinates,¹² and our own experience shows that the effect of choosing different sets is primarily expressed in the low frequency part of the vibrational spectrum. Nonetheless, internal coordinates must be selected with care to assure reliable results. Second, comparing the TEDs from two molecules does not strictly result in a quantitative comparison. In our experience with parabenzoquinones,^{13–17} for instance, there are vibrational modes in both the neutral and the radical anion species that involve strong mixing between the C=C and C=O stretches, with some of these modes essentially 1:1 in energetic contribution. A comparison of the TED analysis in these cases is uninformative because of its most serious shortcoming: information about the phase of the atomic displacements is not taken into account, and only a qualitative visual analysis provides a final determination.

Because of the importance of comparing vibrational normal modes, and because of the limitations of TED analysis for this purpose, we have developed a simple but effective technique for giving fast, quantitative comparisons between the calculated normal modes of similar systems that takes into account the vibrational phases and does not require the user to select a set of internal coordinates. Our method, ViPA (for *V*ibrational *P*rojection *A*nalysis), treats normal modes as simple vectors that define an orthonormal vector space, and projects the modes of another molecule onto this vector space to make the quantitative comparison. This procedure is a generalization of the

work by Duschinsky²⁰ to include comparisons of molecules with different numbers of atoms.

We have made available a simple software routine for performing vibrational projection analysis²¹ and we now present a description of the theory behind the program and show how it can be used to facilitate the quantitative comparison of the normal modes of benzene, phenol, phenol-*d*5, and phenol radical cation. These examples were chosen because the classical Wilson modes of benzene²² have become the standard for describing and comparing the vibrational modes of planar six-membered rings with various substitution patterns.^{23,24} Thus, we demonstrate that ViPA is superior to TED analysis for mode comparisons. Vibrational analysis using ViPA need not be limited to cases of perturbations by chemical substitution, isotopic masses, and different oxidation states, as in the examples we present here; the technique could also be used to compare modes calculated with different methods and/or basis sets and even to compare modes from molecules in different electronic states, which may make it possible to estimate Franck–Condon factors, which are related to the similarity of vibrational wave functions of the ground and excited states of a molecule.²⁵ Additionally, normal modes may be calculated for systems perturbed by noncovalent contacts—including individual molecules, proteins, polymers, and a variety of solid-state systems—so we anticipate that ViPA may become a useful tool for analyzing the vibrational modes of many different structural types.

Theory and Method

The classical theory of vibrations for polyatomic molecules²⁶ demonstrates that a nonlinear N -atom molecule has $3N$ degrees of freedom, where 6 degrees of freedom account for the rotation and translation of the entire molecule, and the remaining $3N - 6$ describe internal vibrations. Each degree of freedom is associated with a single normal mode. If the displacements are given in terms of mass-weighted Cartesian displacements, q_i , where

$$q_i = m_i^{1/2}(x_i^0 - a_i) \quad (1)$$

x_i^0 is the equilibrium position, a_i is the amount of displacement, and m_i is the mass of the atom, then the normal modes form an orthonormal basis set

which spans the space of possible nuclear motions. (Throughout this discussion, elements of matrices are represented by lower-case subscript variables, whereas vectors and matrices themselves are represented by upper-case variables with single or double underlining, respectively.) The $3N \times 3N$ symmetric force constant matrix $\underline{\underline{F}}$ is easily constructed using analytical gradient technique¹ in chemistry programs such as Gaussian-94,²⁷ and we do not reiterate it here.

Once $\underline{\underline{F}}$ is obtained, diagonalization routines such as the Jacobi or Givens–Householder methods^{28,29} may be applied to determine the set of eigenvectors (normal modes), $\underline{\underline{Q}}$, and their corresponding eigenvalues (vibrational frequencies), λ_{3N} . Each eigenvector, $\underline{\underline{Q}}_j$, is a $3N \times 1$ -column vector that defines a single normal mode j . As mentioned earlier, if we use mass-weighted Cartesian displacement coordinates, the resulting eigenvectors are normalized and orthogonal; that is:

$$\underline{\underline{Q}}_j^T \underline{\underline{Q}}_k = \delta_{jk} \quad \delta_{jk} = 1 \quad \text{if } j = k \text{ and} \quad (2)$$

$$\delta_{jk} = 0 \quad \text{if } j \neq k$$

The set of vectors containing the mass-weighted atomic displacements of each normal mode then define a $3N$ -dimensional orthonormal vector space, and any arbitrary vector $\underline{\underline{P}}$ can be projected onto this vector space as:

$$\underline{\underline{P}}_Q = \sum_{j=1}^{3N} p_j \underline{\underline{Q}}_j \quad (3)$$

where the coefficients p_j are defined by:

$$p_j = \underline{\underline{P}}^T \underline{\underline{Q}}_j \quad (4)$$

and the subscript Q denotes that this is a projection of $\underline{\underline{P}}$ on $\underline{\underline{Q}}$, and not necessarily equal to $\underline{\underline{P}}$ itself. The length, or norm, of the projection of $\underline{\underline{P}}$ is given by:

$$\|\underline{\underline{P}}\|_Q^2 = \sum_{j=1}^{3N} p_j^2 \quad (5)$$

For the present application, we do not use just an arbitrary vector $\underline{\underline{P}}$, but will instead use a normal mode from a second molecule with N' atoms, with its own set of normal modes denoted here as $\underline{\underline{Q}}'$. The assumption is made that for each atom in the basis molecule, there is a corresponding atom in roughly the same location relative to the other atoms in the second molecule, and that the atomic

displacement coordinates of the first N atoms of both molecules are ordered similarly before constructing $\underline{\underline{F}}'$. It is not necessary that $N = N'$, only that $N \leq N'$. A complete projection of each mode $\underline{\underline{Q}}'_k$ onto the vectors $\underline{\underline{Q}}_j$ results in a $3N \times 3N'$ matrix, which we denote here as $\underline{\underline{C}}$, whose elements c_{kj} would be defined by:

$$c_{kj} = \underline{\underline{Q}}'_k{}^T \underline{\underline{Q}}_j \quad (6)$$

Because the individual normal modes $\underline{\underline{Q}}'_k$ are normalized by the condition described in eq. (2), eq. (5) shows that:

$$\|\underline{\underline{Q}}'_k\|_Q^2 = \sum_{j=1}^{3N} c_{kj}^2 \cong 1 \quad (7)$$

and the percentage contribution of each normal mode j of the basis molecule to each normal mode k of the second molecule is simply:

$$c_{kj}^{\%} = 100 c_{kj}^2 \quad (8)$$

Because the second molecule may have a greater number of atoms than the basis molecule, or may differ in some other way, there could be some displacements that are not describable in the basis defined by the first molecule. For each normal mode k in the second molecule, we define the deficit by a d -factor, $d_{kj}^{\%}$, as the percent that is not represented by the basis molecule by:

$$d_{kj}^{\%} = 100 - c_{kj}^{\%} \quad (9)$$

Vector projection analysis results are not difficult to interpret: any mode of the second molecule may be described as a linear combination of modes from the basis molecule, with the d -factor, $d_{kj}^{\%}$, representing the percentage not described by the basis molecule. This procedure essentially automates the process of matching modes between similar molecules, as one may determine a match by looking for the basis mode that contributes the highest percentage to the mode of interest in the second molecule.

All quantum calculations in this work were performed using the Gaussian-94 program package and the hybrid Hartree–Fock/density functional method Becke3LYP (B3LYP)³⁰ with a 6-31G(d)^{31,32} basis set. Total energy distributions were obtained using the GAMESS quantum chemistry program with the force constant matrix generated by Gaussian-94. Internal coordinate sets for total energy distributions were chosen using the procedure described by Boatz and Gordon.¹² Vi-

brational projection analysis was performed using the ViPA program, which has been described and made available elsewhere.²¹ It should be noted that the ViPA algorithm uses only the force constant matrix from the quantum calculations and determines normal modes internally, primarily because the modes output by Gaussian-94 are not computed using the mass-weighted Cartesian displacement coordinates, and are therefore not orthogonal, which is an important property in the function of the ViPA method [see eq. (2) and subsequent discussion].

Results and Discussion

As a concrete example of the power of ViPA, we present here a comparison of the normal modes of benzene, phenol, phenol-*d*5, and phenol radical cation, designed to model the perturbation of masses and vibrational force constants by virtue of different chemical substituents, differing isotopic masses, and different oxidation states. This particular set of example molecules was chosen for several additional reasons. First, benzene is a ubiquitous substructure in many organic molecules, and Wilson's classic 1934 study²² has made its vibrational modes the standard by which vibrations of similar structures are described.^{23,24} Second, phenol is a simple perturbation (by chemical substitution) of benzene, it represents a typical monosubstituted benzene derivative, and its vibrational modes have been well characterized experimentally^{33–35} and theoretically^{36–38} in terms of the modes of benzene. Next, we show that changes in vibrational modes due to the ubiquitous expedient of isotopic substitution are easily characterized by comparing the vibrations of phenol-*d*5 to phenol. Last, as an example of the usefulness of ViPA for molecules that differ in oxidation state, we compare the modes of phenol radical cation (a system familiar to our research group³⁹) to those of phenol.

Because the thrust of this work is in demonstrating a new way to analyze the vibrational data obtained from computational techniques, we only briefly discuss the calculated geometries (see Fig. 1). Benzene, because of its fundamental importance and high symmetry, has been studied using numerous techniques, and our calculated bond distances of 1.396 Å for the aromatic C—C bonds and 1.087 Å for C—H bonds agree quite well with previous theoretical⁴⁰ and experimental⁴¹ results.

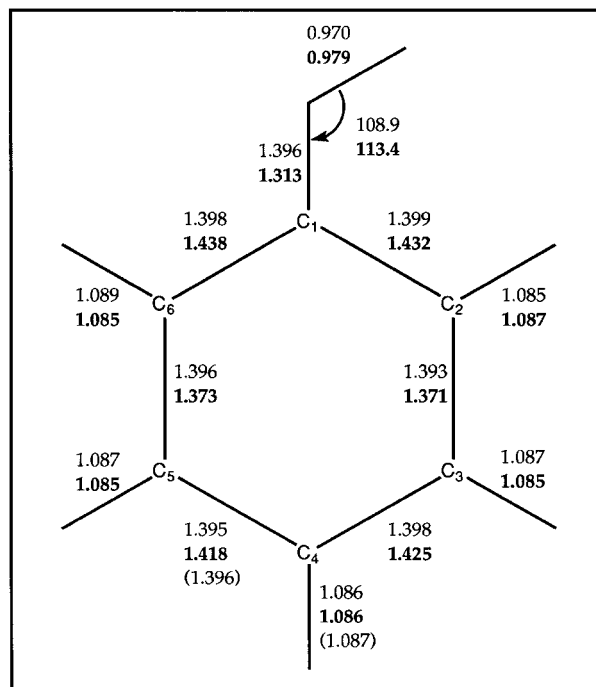


FIGURE 1. Atom numbering and calculated geometries for phenol, phenol radical cation (in bold), and benzene (in parentheses). Bond distances are given in angstroms, and the C—O—H bond angle is reported in degrees.

The molecular geometries of phenol and phenol radical cation have been studied theoretically by others^{36,37,42–44} and our own group³⁹ using computational methods similar to those used here, and again, our calculated geometries are sufficiently close to those and to experimental results^{45,46} that we do not address them further.

The vibrational spectra of phenol and phenol radical cation have been studied extensively both experimentally and theoretically using a variety of techniques including the B3LYP HF/DF method. Although it has been shown that the B3LYP method [with the 6-31G(d,p) basis set, slightly larger than the one used in this work] can reproduce phenol vibrational frequencies with accuracy comparable to MP2 calculations,³⁸ some disagreement remains in the literature about the ability of HF/DF methods to predict some vibrational frequencies in the related phenoxyl radical.⁴⁷ So because the quantum calculations presented here are at a modest level of theory, we do not suggest that the present work be used as a basis for reassigning the vibrational spectra, and are instead concerned only with demonstrating the effectiveness of the ViPA technique in quickly and quantitatively ana-

TABLE I.
Decomposition of Normal Modes of Phenol into Normal Modes of Benzene by Vibrational Projection Analysis.

Phenol		Decomposition into Benzene Modes (Major Contributions Only)	<i>d</i> -Values	Mode Description
Mode	(cm ⁻¹)			
ν_1	234	20.7% 16a + 16.6% rot. + 13.5% 16b	3.9	C—O, ring boat
ν_2	357	2.8% 10a	89.7	C—O—H wag
ν_3	407	22.1% rot. + 17.3% 5 + 11.0% 18b	10.2	C—O bend
ν_4	422	62.9% 16b + 36.8% 16a	0.2	Ring deformation
ν_5	518	35.6% 16a + 24.9% 10b + 20.2% 16b	0.2	Ring boat
ν_6	536	65.1% 6a + 7.0% 7a + 5.2% 20b	1.9	C—C—C Bend
ν_7	633	89.1% 6b	0.2	C—C—C Bend
ν_8	700	77.1% 4 + 22.1% 11	0.0	Ring chair
ν_9	763	36.6% 11 + 23.6% 10a + 13.6% 10b	0.1	C—H wag
ν_{10}	824	56.7% 10b + 34.6% 10a	0.3	C—H wag
ν_{11}	833	25.5% 6a + 23.5% 1 + 15.9% 12	0.9	C—C—C bend
ν_{12}	885	32.7% 17a + 21.7% 10b + 15.5% 17b	0.0	C—H wag
ν_{13}	952	55.2% 17b + 37.6% 17a	0.0	C—H wag
ν_{14}	980	70.0% 5 + 17.3% 17b + 10.6% 17a	0.0	C—H wag
ν_{15}	1015	63.6% 12 + 33.6% 1	0.1	C—C—C bend
ν_{16}	1053	60.2% 18a + 21.5% 1 + 14.3% 18b	0.0	C—H bend
ν_{17}	1104	57.9% 18b + 15.1% 18a + 13.0% 9b	3.1	C—H bend
ν_{18}	1188	70.1% 15 + 23.4% 9b	1.4	C—H bend
ν_{19}	1202	95.4% 9a	0.3	C—H bend
ν_{20}	1212	27.2% 9b	50.4	O—H bend
ν_{21}	1305	17.5% 1 + 13.3% 12 + 10.9% 7a	3.2	C—O stretch
ν_{22}	1368	66.7% 14 + 31.5% 3	0.0	C—C stretch
ν_{23}	1386	50.5% 3 + 25.2% 14	19.2	C—H, O—H bends
ν_{24}	1521	82.9% 19b	4.8	C—C stretch
ν_{25}	1551	85.7% 19a	1.8	C—C stretch
ν_{26}	1657	96.0% 8b	2.0	C—C stretch
ν_{27}	1670	95.6% 8a	1.5	C—C stretch
ν_{28}	3164	37.1% 7b + 30.9% 13 + 22.0% 20b	0.0	C—H stretch
ν_{29}	3185	44.4% 13 + 33.1% 7a + 17.7% 15	0.0	C—H stretch
ν_{30}	3194	37.3% 7b + 24.6% 20b + 22.8% 20a	0.0	C—H stretch
ν_{31}	3209	52.6% 20a + 15.8% 20b + 14.8% 7a	0.0	C—H stretch
ν_{32}	3217	54.3% 2 + 14.3% 20a + 13.0% 20b	0.0	C—H stretch
ν_{33}	3751	1.5% 5	94.2	O—H stretch

lyzing the vibrational modes with respect to similar molecules.

A decomposition of the normal modes of phenol into the Wilson modes of benzene by the ViPA method is presented in Table I. Of the 33 vibrational normal modes of phenol, 20 are seen to be at least 50% comprised of a single benzene Wilson mode, making their assignment and interpretation quite simple. Three more of the phenol modes (ν_2 , ν_{20} , and ν_{33}) are not well described by the basis set formed from benzene normal modes, as can be seen from their high (> 50%) *d*-factor values, and are not surprisingly found to be the torsional, bending, and stretching modes associated with the oxygen-bound hydrogen. The remaining 10 modes

are shown to be a mixture of at least 3 benzene Wilson modes.

Three of the five C—H stretching modes of phenol are described as a substantial mixing between at least three Wilson modes of benzene. Because of the mixed nature of the C—H stretching modes of phenol, and because of the ease with which they may be described graphically and numerically (the modes are composed almost entirely of C—H stretching according to TED analysis), we use them as an example to show some of the advantages of using ViPA over TED to compare vibrational modes. Table II gives a breakdown of the results of TED analysis of the C—H stretching modes of benzene as compared to those of phenol,

phenol-*d*5, and phenol radical cation (where the C—O stretch is included for completeness in place of the congruent C—H stretch). It is immediately clear that, based only on TED analysis, even the six C—H stretching modes of benzene are separable only into indistinguishable pairs of vibrations. To determine the difference between the modes in a pair, it is necessary to look at the individual atomic displacements, either numerically (see Table III) or graphically (as in Fig. 2). Assigning the C—H vibrational modes of phenol (or those of the related species) to Wilson modes based only on the respective TEDs listed in Table II would be almost arbitrary. Comparing the C—H(D) stretching modes of phenol and phenol-*d*5 using only TED results turns out to be quite simple, without the need to resort to atomic displacements, but a quantitative comparison is still not possible using only TEDs. The assignment of the C—H stretching modes of phenol radical cation to the corresponding modes of phenol based on TEDs only is also complicated. The highest and lowest C—H stretching modes of phenol radical cation are clearly

assignable to the respective modes of phenol, but the middle three modes show a higher degree of mixing which makes reliable assignment difficult based only on TED analysis.

It is because of the frequent need to examine vibrational modes graphically to make correct comparisons that we developed the ViPA method to automate and quantify the procedure. In the examples presented here, it is largely a lack of phase information that renders TED analysis difficult, if not impossible, to use in matching modes from similar molecules. ViPA accounts for the phase of relative motions, making comparison much simpler. Comparing Table II with Table III, which contains the mass-weighted cartesian displacements of the C—H(D or O) stretches of our example systems (most of which are also shown graphically in Fig. 2), shows plainly that, in benzene, where TED gives identical results for pairs of vibrations, the displacements differ by a change in sign, or phase, inside these pairs, providing the distinguishing feature. Using these displacements as vectors in ViPA (as described in Theory and

TABLE II. Total Energy Decomposition (TED) for C—H Stretching Modes of Benzene, Phenol Phenol-*d*5, and Phenol Radical Cation.

	C1—H(O)	C2—H	C3—H	C4—H	C5—H	C6—H
Benzene						
3174	.17	.17	.17	.17	.17	.17
3183	.00	.25	.25	.00	.25	.25
3183	.33	.08	.08	.33	.08	.08
3199	.33	.09	.08	.33	.09	.08
3199	.00	.24	.25	.00	.24	.25
3210	.17	.17	.17	.17	.17	.17
Phenol						
3165	.00	.90	.09	.00	.00	.00
3186	.00	.04	.14	.29	.49	.04
3194	.00	.05	.55	.04	.31	.04
3209	.00	.01	.18	.54	.03	.24
3217	.00	.00	.03	.12	.17	.67
Phenol- <i>d</i> 5						
2336	.00	.74	.19	.03	.01	.00
2350	.00	.11	.05	.28	.47	.07
2361	.00	.10	.44	.10	.24	.09
2376	.00	.02	.21	.31	.00	.42
2384	.00	.01	.08	.25	.24	.38
Phenol ^{•+}						
3210	.00	.94	.05	.00	.00	.00
3227	.00	.02	.12	.66	.16	.03
3235	.00	.01	.20	.05	.37	.36
3239	.00	.02	.59	.20	.00	.19
3245	.00	.00	.04	.08	.46	.41

TABLE III.
Mass-Weighted Cartesian Displacements of Hydrogens in C—H Stretching Normal Modes of Benzene, Phenol, Phenol-*d*5, and Phenol Radical Cation.

	H1(O)			H2			H3			H4			H5			H6		
	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
Benzene																		
3174	.00	.39	.00	-.34	-.20	.00	.34	-.20	.00	.00	.39	.00	-.34	-.20	.00	.34	-.20	.00
3183	.00	-.06	.00	.44	.25	.00	-.39	.22	.00	.00	.06	.00	-.44	-.25	.00	.39	-.22	.00
3183	.00	-.55	.00	.20	.12	.00	.28	-.16	.00	.00	.55	.00	-.20	-.12	.00	.28	.16	.00
3199	.00	-.28	.00	.23	.14	.00	.48	-.28	.00	.00	-.28	.00	.23	.14	.00	.48	-.28	.00
3199	.00	-.48	.00	-.42	-.24	.00	.00	.01	.00	.00	-.48	.00	-.42	-.24	.00	.00	.01	.00
3210	.00	.39	.00	.34	.20	.00	.34	-.20	.00	.00	-.39	.00	-.34	-.20	.00	-.34	.20	.00
Phenol																		
3165	.00	.00	.00	-.80	-.44	.00	.25	-.14	.00	.00	.06	.00	-.04	-.02	.00	.01	.00	.00
3186	.00	.00	.00	.16	.09	.00	.32	-.18	.00	.01	.52	.00	-.58	-.33	.00	.17	-.10	.00
3194	.00	.00	.00	-.18	-.10	.00	-.62	.36	.00	.00	-.19	.00	-.47	-.26	.00	.17	-.10	.00
3209	.00	.00	.00	-.08	-.05	.00	-.35	.20	.00	.01	.70	.00	.14	.07	.00	-.40	.24	.00
3217	.00	.00	.00	.04	.02	.00	.14	-.08	.00	.00	-.34	.00	-.34	-.19	.00	-.67	.41	.00
Phenol- <i>d</i> 5																		
2336	.00	.00	.00	-.69	-.38	.00	.35	-.19	.00	.00	.16	.00	-.10	-.06	.00	.03	-.02	.00
2350	.00	.00	.00	-.26	-.15	.00	-.18	.11	.00	-.01	-.48	.00	.55	.31	.00	-.21	.12	.00
2361	.00	.00	.00	-.25	-.15	.00	-.52	.31	.00	.01	-.29	.00	-.40	-.21	.00	.24	-.14	.00
2376	.00	.00	.00	-.11	-.07	.00	-.37	.21	.00	.01	.51	.00	-.03	-.03	.00	-.51	.31	.00
2384	.00	.00	.00	-.06	-.04	.00	-.23	.13	.00	.00	.46	.00	.39	.22	.00	.48	-.30	.00
Phenol ^{•+}																		
3210	.00	.00	.00	.80	.48	.00	-.18	.11	.00	.00	-.05	.00	.02	.01	.00	.00	.00	.00
3227	.00	.00	.00	.11	.07	.00	.29	-.18	.00	.00	.78	.00	-.33	-.20	.00	.15	-.09	.00
3235	.00	.00	.00	-.08	-.05	.00	-.37	.22	.00	.00	-.22	.00	-.50	-.30	.00	.49	-.31	.00
3239	.00	.00	.00	.12	.08	.00	.63	-.38	.00	.00	-.43	.00	.01	.01	.00	.35	-.22	.00
3245	.00	.00	.00	.03	.02	.00	.16	-.10	.00	.00	-.27	.00	-.56	-.33	.00	-.52	.33	.00

Method) allows us to say that ν_{28} of phenol, a C—H stretching mode, can be described as 37.1% Wilson mode 7b of benzene, 30.9% mode 13, and 22.0% mode 20b. Although such phenol modes could be exclusively assigned to the highest Wilson mode contributor, we believe that, given the quantitative decomposition from ViPA, it is most accurate simply to state each major contributor and its relative contribution. So the ViPA method allows us to make quick and accurate descriptions of the C—H stretching modes of phenol relative to the modes of benzene, whereas TED alone would have confirmed only that these five modes are indeed C—H stretches.

Table IV presents the results of ViPA decomposition of the vibrational modes of phenol-*d*5 into the modes of phenol. As noted earlier with respect to the C—H stretching frequencies, TED analysis can often provide enough data to match modes in isotopically substituted compounds with those of their parent species (albeit only qualitatively). This relative ease of comparison is reflected with ViPA

in Table IV by the fact that only 5 of the 33 vibrational modes of phenol-*d*5 have a maximum contribution of less than 50% from a phenol mode. These five modes show a large degree of mixing of various phenol torsional and bending modes involving hydrogens, as would be expected upon deuteration. These five modes are not best characterized as matching a single mode of phenol, but instead should be described by their exact contributions, which in all five cases would consist of at least two and sometimes three mixed modes of phenol. Overall, ViPA makes the matching of deuterated modes virtually automatic, which can save a great deal of visual analysis time, especially with larger, more complex systems.

Another case in which mode comparison is frequently essential involves molecules in different oxidation states. As an example of the continued utility of ViPA in this situation, we provide in Table V the results of a decomposition of the vibrational modes of phenol radical cation into the modes of phenol. Here, unlike the earlier case of

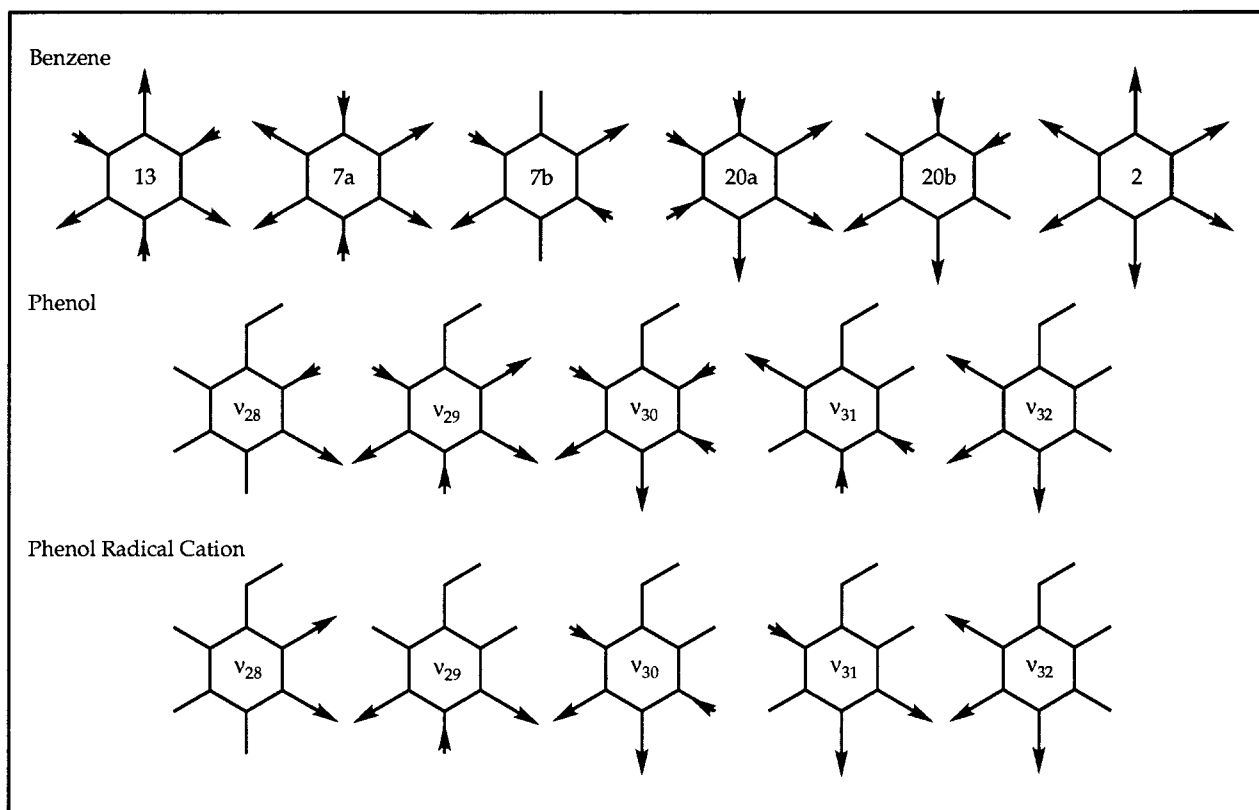


FIGURE 2. Qualitative graphic representations of the hydrogen displacements in the C—H stretching normal modes calculated for benzene, phenol, and phenol radical cation. A complete listing of the normal modes for each molecule (including phenol-*d*5) may be found in Tables VI–IX in the Supplemental Material.

deuteration, the atomic masses remain unchanged, while the structural and bonding properties differ. As can be seen in Table II with just the C—H stretching modes, this makes the process of matching modes using only TED analysis much more difficult. But as the information in Table IV demonstrates, ViPA makes the process quite easy, with all but two modes having primary contributions of over 50% from individual phenol modes. The two that do not (ν_{21} and ν_{23} of phenol radical cation) are seen to be the result of near 1:1 mixing of phenol modes ν_{22} and ν_{23} . A brief glance down the table makes it readily apparent which vibrational modes have shifted upon electron loss, the most significant being the ν_2 C—O—H torsional mode of phenol at 357 cm^{-1} (shifted upward to 613 cm^{-1} phenol radical cation), the ν_{20} C—O—H bend at 1212 cm^{-1} (shifted downward to 1155 cm^{-1} in phenol radical cation), and the ν_{21} C—O stretch at 1305 cm^{-1} (shifted upward to 1406 cm^{-1} in phenol radical cation). A visual analysis of the modes in combination with TED results for even this relatively small system would require sub-

stantially more time to achieve qualitatively what ViPA provides quantitatively in only a few moments.

Conclusions

We have demonstrated the theory and the practice of vibrational projection analysis (ViPA) for several simple systems. We have shown that the method can be used to assign quickly and quantitatively the vibrational normal modes of molecules in terms of the normal modes of classical parent molecules such as benzene, which can aid in the interpretation of the effects of chemical substitution on vibrational spectra. We have also demonstrated that ViPA can be used to interpret the results of isotopic substitution on molecular vibrations efficiently. The example of phenol radical cation was used to demonstrate that ViPA is also useful in cases where bonding and oxidation states have changed, a situation common in studies involving electron transfer in materials and biologi-

TABLE IV.
Decomposition of Normal Modes of Phenol-d5 into Normal Modes of Phenol and Benzene by Vibrational Projection Analysis.^a

Phenol-d5 Mode	(cm ⁻¹)	Decomposition into Phenol Modes (Major Contributions Only)	Benzene Normal Mode with Largest Contribution
ν_1	220	97.5% ν_1	23.7% 16a
ν_2	354	94.8% ν_2	6.5% 16a
ν_3	371	89.0% ν_4	57.7% 16b
ν_4	389	98.1% ν_3	22.0% 9b
ν_5	443	84.7% ν_5	54.9% 11
ν_6	522	98.4% ν_6	66.3% 6a
ν_7	563	59.9% ν_9 + 21.7% ν_9 + 11.5% ν_{14}	33.9% 4
ν_8	607	97.3% ν_7	85.9% 6b
ν_9	633	46.4% ν_9 + 21.5% ν_{12} + 13.0% ν_{10}	63.4% 10a
ν_{10}	645	83.6% ν_{10}	81.0% 10b
ν_{11}	754	60.2% ν_{12} + 14.6% ν_{14} + 11.2% ν_9	45.1% 17b
ν_{12}	768	88.7% ν_{13}	53.0% 17a
ν_{13}	771	73.2% ν_{11} + 15.3% ν_{16}	31.7% 18a
ν_{14}	803	63.3% ν_{14} + 23.2% ν_8	61.1% 5
ν_{15}	835	57.0% ν_{17} + 27.9% ν_{18}	47.7% 15
ν_{16}	855	38.0% ν_{19} + 37.2% ν_{16}	32.7% 9a
ν_{17}	862	56.7% ν_{18} + 23.7% ν_{17}	53.2% 9b
ν_{18}	893	52.5% ν_{19} + 22.3% ν_{16} + 18.6% ν_{11}	51.4% 9a
ν_{19}	974	93.5% ν_{15}	56.7% 12
ν_{20}	1042	32.8% ν_{23} + 30.1% ν_{20} + 26.4% ν_{22}	75.1% 3
ν_{21}	1219	36.2% ν_{20} + 32.0% ν_{21}	12.0% 19a
ν_{22}	1239	44.1% ν_{21} + 17.2% ν_{20} + 12.6% ν_{23}	17.3% 19a
ν_{23}	1366	56.7% ν_{22} + 37.1% ν_{23}	87.2% 14
ν_{24}	1417	79.7% ν_{24}	58.0% 19b
ν_{25}	1453	80.1% ν_{25}	48.6% 19a
ν_{26}	1626	92.1% ν_{26}	85.7% 8b
ν_{27}	1639	92.6% ν_{27}	85.0% 8a
ν_{28}	2336	93.1% ν_{28}	43.8% 13
ν_{29}	2350	93.1% ν_{29}	34.2% 7b
ν_{30}	2361	93.0% ν_{30}	32.4% 20b
ν_{31}	2376	87.2% ν_{31}	74.5% 20a
ν_{32}	2384	89.1% ν_{32}	66.5% 2
ν_{33}	3751	100% ν_{33}	1.5% 9b

^aAll *d*-values for the phenol-d5-to-phenol comparison were 0.0 and so are not reported. The *d*-values associated with the phenol-d5-to-benzene comparison are similar to those reported in Table I for the phenol-to-benzene decomposition.

cal chemistry. Total energy distributions, a common method for describing the modes of a single molecule in terms of its internal coordinates, is shown to be less useful when attempting to compare modes of different molecules, primarily because it fails to take into account phase information, but also because the resulting comparisons give only a qualitative idea of the mixing of various modes from the parent system.

We have recently made available a simple program for performing the analysis, and anticipate that the ViPA method will be widely applied in a variety of situations. For instance, vibrational nor-

mal modes can be determined for a variety of systems using a variety of methods. ViPA could be used to analyze the vibrational normal modes calculated for systems such as ordered solids, large proteins, or polymers based on molecular mechanics normal modes. ViPA may also find application in determining Franck–Condon factors, which are determined based on a comparison of the vibrational wave functions of ground and excited state systems, a situation quite similar to the case of different oxidation states presented in this work. In a more theoretical aspect, ViPA might be used to evaluate the quality of various computational

TABLE V.
Decomposition of Normal Modes of Phenol⁺⁺ into Normal Modes of Phenol and Benzene by Vibrational Projection Analysis.^a

Mode	Phenol ⁺⁺ (cm ⁻¹)	Decomposition into Phenol Modes (Major Contributions Only)	Benzene Normal Mode with Largest Contribution
ν_1	187	99.9% ν_1	21.6% 16a
ν_2	363	98.3% ν_4	61.3% 16b
ν_3	414	98.1% ν_3	19.9% rot.
ν_4	438	81.7% ν_5	32.5% 16a
ν_5	526	99.4% ν_6	68.0% 6a
ν_6	569	96.4% ν_7	78.1% 6b
ν_7	613	93.5% ν_2	6.6% 10a
ν_8	624	77.9% ν_9 + 17.1% ν_5	52.4% 11
ν_9	795	72.3% ν_9 + 23.5% ν_{10}	44.2% 10b
ν_{10}	806	67.7% ν_{10} + 21.2% ν_9	35.1% 10a
ν_{11}	822	96.5% ν_{11}	30.3% 1
ν_{12}	945	91.5% ν_{12}	38.9% 17a
ν_{13}	994	65.0% ν_{15} + 32.6% ν_{16}	51.2% 1
ν_{14}	1000	63.0% ν_{16} + 33.6% ν_{15}	40.2% 12
ν_{15}	1001	98.5% ν_{13}	64.5% 17b
ν_{16}	1018	96.4% ν_{14}	71.4% 5
ν_{17}	1108	92.0% ν_{17}	47.6% 18b
ν_{18}	1155	66.2% ν_{20} + 23.2% ν_{18}	46.4% 9b
ν_{19}	1200	68.5% ν_{15} + 24.5% ν_{20}	64.5% 15
ν_{20}	1213	96.1% ν_{19}	86.6% 9a
ν_{21}	1376	48.5% ν_{22} + 46.8% ν_{23}	77.3% 3
ν_{22}	1406	85.3% ν_{21}	33.4% 19a
ν_{23}	1419	47.7% ν_{23} + 36.9% ν_{22}	73.6% 14
ν_{24}	1461	58.0% ν_{26} + 15.6% ν_{24} + 12.9% ν_{27}	50.8% 8b
ν_{25}	1520	80.6% ν_{25}	61.6% 19a
ν_{26}	1555	72.5% ν_{24}	68.2% 19b
ν_{27}	1668	79.8% ν_{27} + 19.0% ν_{26}	77.4% 8a
ν_{28}	3210	99.2% ν_{28}	35.9% 7b
ν_{29}	3227	84.0% ν_{29}	43.3% 13
ν_{30}	3235	74.8% ν_{30} + 13.4% ν_{31}	56.0% 7b
ν_{31}	3239	77.6% ν_{31} + 18.9% ν_{30}	75.7% 20a
ν_{32}	3245	89.5% ν_{32}	57.1% 2
ν_{33}	3653	99.0% ν_{33}	1.4% 9b

^aAll *d*-values for the phenol⁺⁺-to-phenol comparison were 0.0 and so are not reported. The *d*-values associated with the phenol⁺⁺-to-benzene comparison are similar to those reported in Table I for the phenol-to-benzene decomposition.

methods by comparing the normal modes calculated using one technique to those from some higher- or lower-level calculation. Therefore, we anticipate that ViPA will take its place as a primary tool used by computational chemists to analyze large sets of complicated vibrational modes quickly and quantitatively.

which report the entire ViPA results for each comparison made, are provided as supplemental material. This information is available through the *Journal of Computational Chemistry* website.

Supplementary Material

Tables VI–IX, which contain all mass-weighted Cartesian displacement normal modes of each of the four molecules in this study, and Tables X–XIV,

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